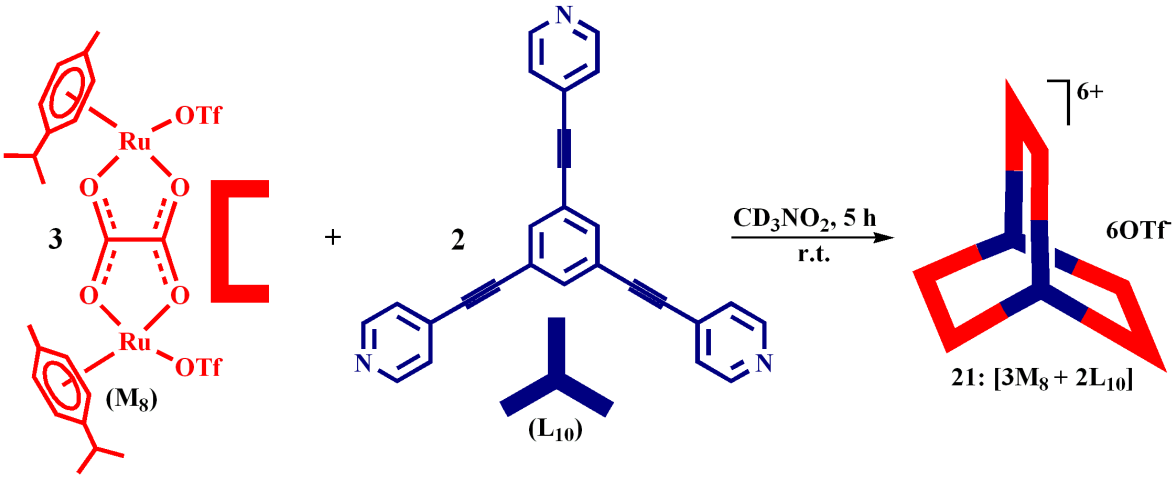
SYNOPSIS

Over the past few decades, supramolecular self-assembly has become an alternative synthetic tool for constructing targeted discrete molecular architectures. Among various interactions, metal-ligand coordination has attracted great attention owing to high bond enthalpy (15−50 Kcal/mol) and predictable directionality. The basic principle of metal-ligand directed self-assembly relies on the proper designing of information encoded rigid complementary building units (a transition metal based acceptor and a multidentate organic donor) that self-recognize themselves in a chemically reasonable way (depends on their bite angle and symmetry) during self-assembly process. As far as acceptor units are concerned, Pd(II) and Pt(II) metal-based cis-blocked 90° acceptors have so far been used greatly for the construction of a library of 2D/3D discrete supramolecular architectures due to their rigid square planar geometry and kinetic lability. However, in some cases the efforts to design finite supramolecular architectures using a cis-blocked 90° acceptor in combination with a bulky donor ligand were unsuccessful, which may be due to the steric demands of donor ligand. Moreover, the resulted assemblies from such cis-blocked 90° building unit are mostly non-fluorescent in nature and limit the possibility of using them as chemosensors for various practical applications.

Unlike that of rigid square-planar Pt(II) and Pd(II)-metal based building blocks, the use of other transition metal-based building units for the construction of discrete nanoscopic molecular architectures are known to lesser extent, mainly because of their versatile coordination geometries. However, some of the half-sandwiched piano-stool complexes of late transition metals like Ru, Os, Ir and Rh are known to maintain the stable octahedral geometry under various reaction conditions. Moreover, the self-assembly using redox active transition metal-based building units may lead to redox active assemblies.

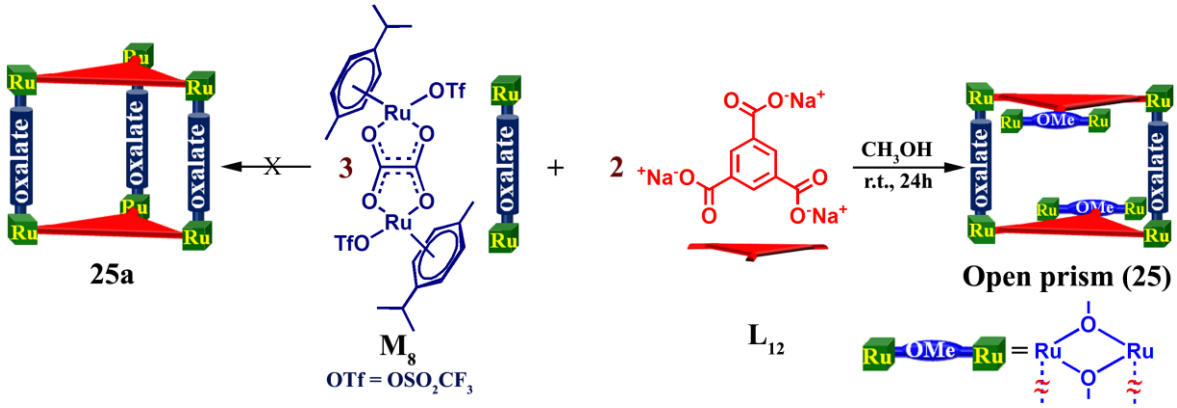
On the other hand, symmetrical rigid donors have been widely used as the favorite choices for the purpose of constructing desired product mainly due to their predictable directionality. Flexible linkers are not predictable in their directionality during self-assembly process and thus results mostly in undesired polymeric products. Furthermore, metal-ligand directed self-assembly provides opportunity to introduce multifunctionality in a single step within/onto the final supramolecular architectures. Among various functional groups, the incorporation of unsaturated ethynyl functionality is expected to enrich the final assemblies to be π-electron-rich and the attachment of ethynyl functionality with heavy transition metal ions are known to be

This chapter also explains the self-sorting of an unusual octanuclear incomplete prism $[Ru_8(\eta^6\text{-}p\text{-cymene})_8(tma)_2(\mu\text{-}\eta^4\text{-}C_2O_4)_2(OMe)_4](CF_3SO_3)_2$ (**25**) *via* ruthenium-oxygen coordination driven self-assembly of building block $\mathbf{M_8}$ and sodium benzene-1,3,5-tricarboxylate ($\mathbf{L_{12}}$) (Scheme 4). Electronic absorption study indicated that prism **25** exhibited a remarkable shape-selective binding affinity for 1,3,5-trihydroxybenzene (phluoroglucinol) *via* multiple hydrogen bonding interactions and such shape-selective binding was confirmed by single crystal X-ray diffraction analysis.



Scheme 3: Schematic representation of the formation of [3 + 2] self-assembled trigonal prismatic cage.

CHAPTER 5 covers the syntheses of a few discrete metallamacrocycles using flexible imidazole/carboxylate based donors instead of much widely employed polypyridyl donors. The metal-ligand directed self-assembly of oxalato-bridged acceptor **M_8** and an imidazole-based tetratopic donor (**L_{11}**; 1,2,4,5-tetrakis(imidazol-1-yl)benzene) in methanol afforded [2 + 1] self-assembled tetranuclear macrocycle **23**. Conversely, the similar combination of **L_{11}** with 2,5-dihydroxy-1,4-benzoquinonato-bridged binuclear complex (**M_9**) in 1:2 molar ratio in methanol resulted in an octanuclear cage **24**. Both the complexes (**23**–**24**) were isolated as their triflate salts in high yields and were characterized by various spectroscopic methods including single crystal X-ray diffraction analysis.

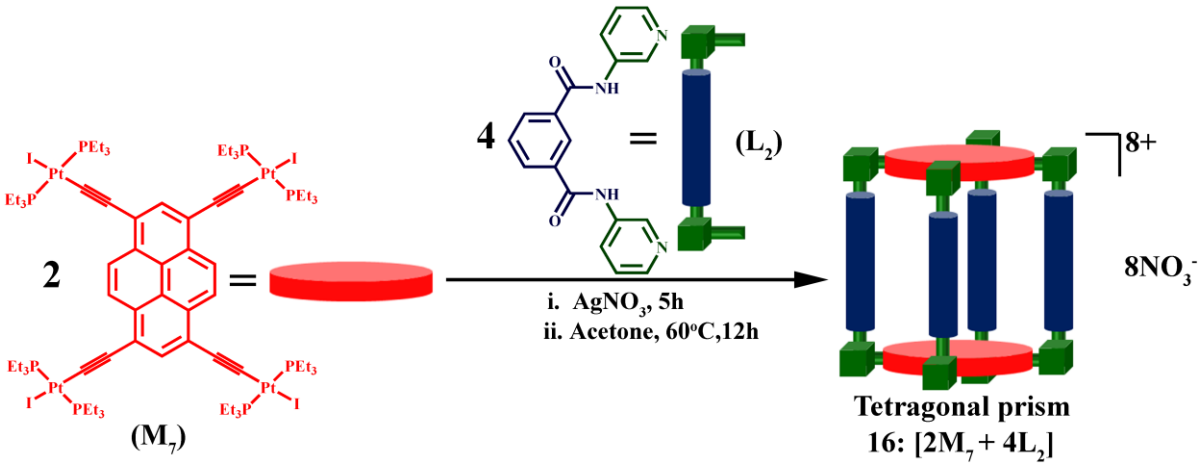


Scheme 4: Schematic representation of formation of an octanuclear incomplete Ru(II) open prism *via* ruthenium-oxygen coordination driven self-assembly.

This chapter also describes two-component coordination [2 + 4] self-assembly of a pyrene-based Pt^{II}_8 tetragonal prism (**16**) as shown in Scheme 2, using a newly designed tetratopic organometallic acceptor (**M_7**; 1,3,6,8-tetrakis[*trans*-$Pt(PEt_3)_2(NO_3)$(ethynyl)]pyrene) in combination with an amide-based "clip" donor (**L_2**) and propensity of this prism (**16**) as a selective fluorescence sensor for nitroaromatic explosives has been examined both in solution as well as in thin-film.

CHAPTER 4 reports the synthesis and structural characterization of a series of Ru(II)-based bi- and tetra-nuclear metallamacrocycles and hexanuclear trigonal prismatic cages. In principle, the self-assembly of a "clip" acceptor with an asymmetrical ditopic donor is expected to give two different linkage isomeric (*head-to-tail* and *head-to-head*) molecular rectangles because of different bond connectivity of the donor. However, the equimolar combination of half-sandwiched *p*-cymene binuclear Ru(II)-based "clip" acceptors (**M_8**–**M_9**) and an amide-based ambidentate donor (**L_6**) resulted in the self-sorting of single linkage (*head-to-tail*) isomeric rectangles **17**–**18** as only products, respectively [**M_8** = $[Ru_2(\mu\text{-}\eta^4\text{-}C_2O_4)(MeOH)_2(\eta^6\text{-}p\text{-cymene})_2](CF_3SO_3)_2$; **$M_9$** = $[Ru_2(\mu\text{-}\eta^4\text{-}C_6H_2O_4)(MeOH)_2(\eta^6\text{-}p\text{-cymene})_2](CF_3SO_3)_2]$. Molecular structures of these *head-to-tail* linkage isomeric rectangles were unambiguously proved by single crystal X-ray diffraction analysis. Likewise, the self-assembly of oxalato-bridged Ru(II) acceptor **M_8** with a rigid dipyridyl "clip" donor **L_8** yielded a tetranuclear cationic pincer complex **19**, while a similar reaction of **M_8** with an anthracene-functionalized "clip" donor **L_9** having shorter distance (between their reactive sites) compared to **L_8** led to the formation of [1 + 1] self-assembled macrocycle **20**. This chapter also represents the design and synthesis of two hexanuclear trigonal prismatic cages (**21**–**22**) from the self-assembly of a π-electron rich tripyridyl donor (**L_{10}**; 1,3,5-tris(4-pyridylethynyl)benzene) in combination with binuclear acceptors **M_8** and **M_9**, respectively (Scheme 3). Formation of these prismatic cages was initially characterized using various spectroscopic techniques and the molecular structure of oxalato-bridged prism **21** was confirmed by single crystal X-ray diffraction analysis. In addition to the structural characterization, the pincer complex **19** and trigonal prismatic cages **21**–**22** were used as fluorescence sensors for nitroaromatic explosives owing to their large internal porosity and their π-electron rich nature.

CHAPTER 3 presents two-component coordination-driven self-assembly of a series of [2 + 2] molecular rectangles and a [2 + 4] self-assembled molecular tetragonal prism. An equimolar combination of pre-designed linear Pt^{II}_2-acceptors **M_5**–**M_6** separately with three different "clip" donors (**L_2, L_8**–**L_9**) led to the formation of [2 + 2] self-assembled tetranuclear cationic molecular rectangles (**10**–**15**), respectively [**M_5** = 1,4-bis[*trans*-$Pt(PEt_3)_2(NO_3)$(ethynyl)] benzene; **M_6** = 4,4'-bis[*trans*-$Pt(PEt_3)_2(CF_3SO_3)$(ethynyl)]biphenyl; **L_8** = 1,3-bis(3-pyridyl)ethynylbenzene; **L_9** = 1,8-bis(4-pyridyl)ethynylanthracene]. Rectangles **10**–**15** showed strong fluorescence in solution owing to their extended π-conjugation. Amide-functionalized rectangle **10** was used as a macrocyclic receptor for dicarboxylic acids. Solution state fluorescence study showed that rectangle **10** selectively binds ($K_{SV} = 1.4 \times 10^4\ M^{-1}$) with maleic acid by subsequent enhancement in emission intensity and addition of other analogous aliphatic dicarboxylic acids such as fumaric, succinic, adipic, mesaconic and itaconic acids causes no change in the emission spectra; thereby demonstrated its potential use as macrocyclic receptor in sensor applications. Since rectangle **15** is enriched with π-conjugation, it was examined as a fluorescence sensor for electron-deficient nitroaromatics such as picric acid, which is often considered as a secondary chemical explosive. The fluorescence study of **15** showed a significant quenching of initial emission intensity upon titrating with picric acid (PA) and it exhibited the largest fluorescence quenching response with high selectivity for picric acid.



Scheme 2: Schematic representation of formation of [2 + 4] self-assembled of molecular tetragonal prism.

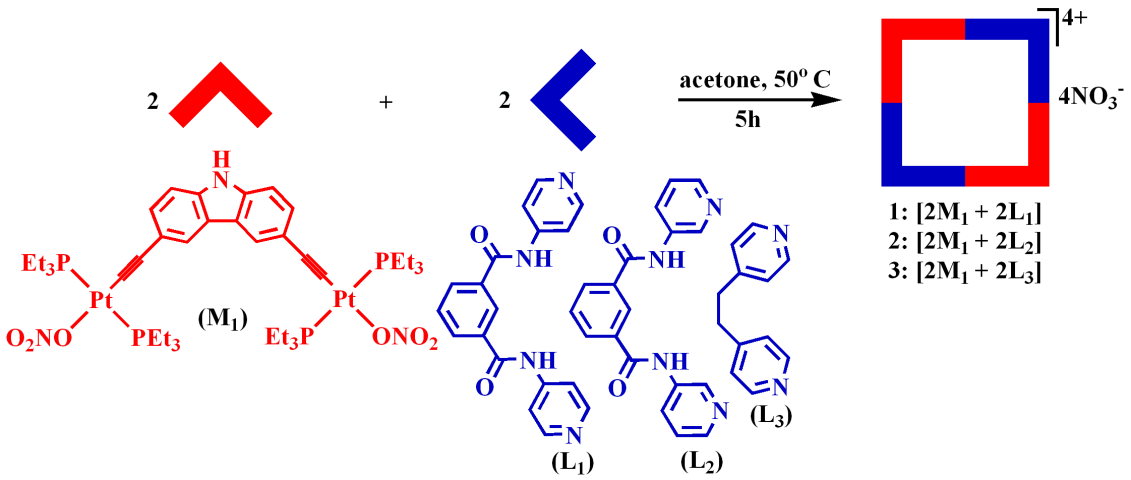
An equimolar (1:1) combination of same acceptor $\mathbf{M_1}$ with rigid linear ditopic donors ($\mathbf{L_4}$–$\mathbf{L_5}$) yielded [4 + 4] self-assembled octanuclear molecular squares **4** and **5**, respectively [$\mathbf{L_4}$ = 4,4'-bipyridine; $\mathbf{L_5}$ = *trans*-1,2-bis(4-pyridyl)ethylene]. Conversely, a similar reaction of $\mathbf{M_1}$ with an amide-based unsymmetrical linear flexible ditopic donor $\mathbf{L_6}$ resulted in the formation a [2 + 2] self-sorted molecular rhomboid (**6a**) as a single product [$\mathbf{L_6}$ = N-(4-pyridyl)isonicotinamide]. Despite the possibility of several linkage isomeric macrocycles (rhomboids, triangles and squares) due to different connectivity of the ambidentate linker, the formation of a single and symmetrical molecular rhomboid **6a** as an exclusive product is an interesting observation. This chapter also presents the synthesis and characterization of a complementary 90° dipyridyl donor 3,6-bis(4-pyridylethynyl)carbazole ($\mathbf{L_7}$). Stoichiometric combination of $\mathbf{L_7}$ with several Pd^{II}/Pt^{II}-based 90° acceptors ($\mathbf{M_2}$–$\mathbf{M_4}$) yielded [2 + 2] self-assembled molecular "bowl" shaped macrocycles (**7**–**9**) respectively, in good yields [$\mathbf{M_2}$ = *cis*-(dppf)Pd$(CF_3SO_3)_2$; $\mathbf{M_3}$ = *cis*-(dppf)Pt$(CF_3SO_3)_2$; $\mathbf{M_4}$ = *cis*-(tmen)Pd$(NO_3)_2$]. All these newly synthesized macrocycles were characterized by various spectroscopic techniques and molecular structures of some of them were confirmed by single crystal X-ray diffraction analysis. In addition to their syntheses and characterization, fluorescence chemosensing ability for various analytes was investigated.

Macrocycle **1** is a system composed of amide-based receptor units and carbazole-based fluorophore moieties. The fluorescence study of **1** elicited a dramatic enhancement in the fluorescence intensity upon gradual addition of $P_2O_7^{4-}$ anion in DMF/H_2O solvent mixture, whereas similar titration under identical condition with other anions like F^-, ClO_4^-, and $H_2PO_4^-$ did not show such change. Hence, molecular square **1** can be used as selective fluorescence sensor for pyrophosphate ($P_2O_7^{4-}$) anion. Due to their extended π-conjugation, macrocycles **3**–**4** were used as fluorescence sensors for electron-deficient nitroaromatics, which are the chemical signatures of many commercially available explosives. The fluorescence study showed a marked quenching of initial fluorescence intensity of the macrocycles (**3–4**) upon gradual addition of picric acid (PA) and they exhibited large fluorescence quenching responses with high selectivity for nitroaromatics among various other electron deficient aromatic compounds tested. As macrocycle **7** has large concave aromatic surface, it was utilized as a suitable host for large convex guest such as fullerene C_{60}. The fluorescence quenching titration study suggested that macrocycle **7** forms a stable ~1:1 host-guest complex with C_{60} and the calculated association constant (K_{SV}) is $1.0 \times 10^5\ M^{-1}$.

luminescent in nature due to the facile metal to ligand charge transfer (MLCT). Hence, the final supramolecular complexes can be used as potential fluorescence sensors for electron-deficient nitroaromatics, which are the chemical signature of most of the commercially available explosives. The main thrust of the present investigation is focused on the judicious design and syntheses of multifaceted 2D/3D supramolecular architectures of finite shapes, sizes and functionality using Pt(II)/Ru(II) based "shape-selective" organometallic building blocks and investigation of their application as chemosensors.

CHAPTER 1 of the thesis presents a general review on the core concepts of self-assembly and supramolecular chemistry. In particular, it underlines the importance of metal-ligand directional bonding approach for designing a vast plethora of discrete 2D/3D supramolecular architectures with tremendous variation in topology.

***CHAPTER* 2** describes the design and syntheses of a series of 2D metallamacrocycles using carbazole-functionalized shape-selective 90° building units. A new Pt_2^{II} organometallic 90° acceptor 3,6-bis[*trans*-$Pt(PEt_3)_2(NO_3)$(ethynyl)]carbazole (**M_1**) containing ethynyl functionality is synthesized *via* Sonagashira coupling reaction and characterized. The combination of **M_1** with three different flexible ditopic donors (**L_1**−**L_3**) afforded [2 + 2] self-assembled molecular squares (**1**−**3**), respectively [where **L_1** = 1,3-bis(4-pyridyl)isophthalamide; **L_2** = 1,3-bis(3-pyridyl)isophthalamide; **L_3** = 1,2-bis(4-pyridyl)ethane] (Scheme 1).



Scheme 1: Schematic presentation of the formation of a series of [2 + 2] self-assembled molecular squares.